



Cutting the Gordian Knot of electrodeposition via controlled cathodic corrosion enabling the production of supported metal nanoparticles below 5 nm



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ABSTRACT

In the past decades, there has been an ongoing search for tailor-made active metal nanoparticles for the use as electrocatalysts. An upcoming versatile and green method for the synthesis of nanoparticles is electrodeposition. However, the state-of-the-art electrodeposited metal particle sizes are in the range of 50–200 nm. Production of high surface area metallic electrocatalysts with small particle sizes is a serious limitation of electrodeposition, i.e., the Gordian Knot. In this article, we present a novel and facile approach by combining electrodeposition with controlled cathodic corrosion to obtain tailor-made nanoparticles down to the single atom. Via controlled cathodic corrosion treatment, relatively big electrodeposited metal nanoparticles (Ag, Pt, Pd, Ni, etc.) are effectively broken down and evenly dispersed on the carbon electrode surface, without particle detachment. The same electrochemical phenomenon is also utilized for in-situ electrocatalysts reactivation, referred as redisposition, of the degraded electrocatalysts. The two new concepts open new possibilities and applications for the electrodeposition as a metal nanoparticles production method and in-situ regeneration solutions for electrochemical energy conversion reactors like fuel cells and electrolyzers; as the two pillars of a near-future transition to sustainable energy.

1. Introduction

Fundamental advances in energy conversion and storage that are full of vigor in meeting outfaces of some environmental phenomena such as global warming and impact of fossil fuels are held by new materials [1,2], particularly nanoparticles that present unique properties as electrocatalysts in many applications such as lithium batteries, solar cells, fuel cells and electrosynthetic processes [3–5]. Nanoparticles are the basic structural blocks in nanotechnology and the starting point in producing nanostructure materials and tools. Commonly used metals in electrocatalysis, sensors, and other electronic devices are precious metals like Pt, Ir, Pd, etc. Due to their scarcity and high value, it is very important to optimise their usage. This is done by production of small nanoparticles due to the enhanced surface to the volume ratio. As a result, there is a strong need for the nanoengineering and nanoscience research [5,6] for economic, in-situ, scalable and environmentally friendly production processes of metallic nanoparticles below 5 nm. Current synthesis methods have at least one of the following issues: energy-intensive, costly, complex or not scalable. A promising method that has the possibility to fulfill all these criteria is

electrochemical metal deposition [7–9]. However, it suffers from an inability to produce nanoparticles below 5 nm.

Electrodeposition is a convenient, fast and versatile technique to obtain nanocrystals on a conductive support material [2,10]. Electrodeposition is performed by applying a potential to an electrode and thus passing a current through an electrochemical cell, reducing a metal ion from the electrolyte to its metallic form [11]. Electrodeposition offers a superior control over the synthesis process since the driving force is the applied potential, a quantity that can be easily and precisely controlled down to the mV and over timescales as short as ns [7,12]. In addition, the low material waste and small capital cost ensure that an economic production process for nanoparticles is created. Of equal importance is the ability to work without any additives apart from metal salts enabling great purity and cleanliness, which is extremely important for optimal electrocatalysts performance. The electron is considered as a cheap, clean and energy efficient reagent and through the absence of contaminants introduced by addition of capping [13] or reducing [14] – agents ensure that electrodeposition is a promising, scalable, green technology for the future with a high perspective [2], [15]. The first electrodeposition experiments were carried out in the 19th century by

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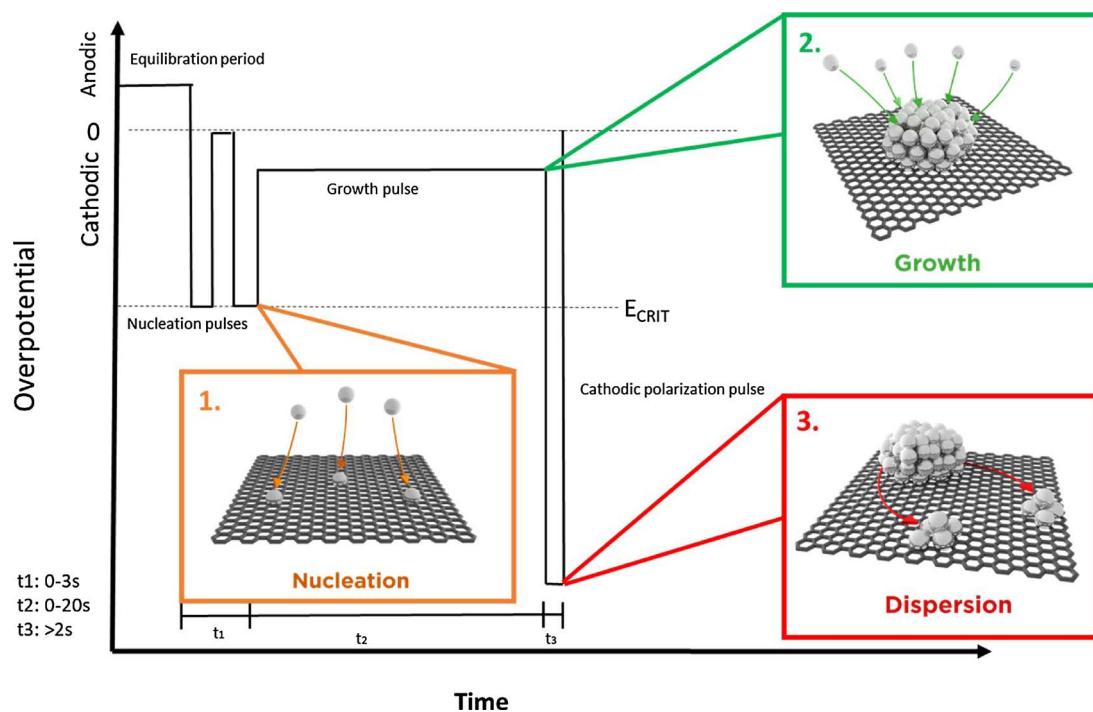


Fig. 1. 3-Step electrodeposition and cathodic polarization scheme.

applying a single potential pulse and resulted in the uncontrolled growth of nanoparticles on the support [8,16]. To increase the control over morphology and particle size, Penner [7] and Plieth [17] adapted the procedure by using a double-pulse approach. The general principle of double-pulse is to separate the nucleation of crystals from the further growth on the surface by applying two individual pulses [18,19]. In the ongoing search for tailor-made, more active electrocatalysts, various attempts have been made to increase the control over nanoparticle size distribution. By performing the electrodeposition in organic solvents [20,21] and lowering the overvoltage of the pulses until a threshold value, the growth kinetics can be slowed down enabling the synthesis of nanoparticles in the range of 100 nm [22,23]. Accurate control over the morphology and the size distribution of metallic nanoparticles is needed to boost their electrocatalytic properties [24–27]. However, larger particle sizes and broader particle distribution of 50–250 nm [18,19,28,29] remain the major bottleneck in the application of electrodeposition that halts the technique's effectiveness compared with classical chemical synthesis, sputtering or biological processes as nanoparticle preparation methods [15,21].

Cathodic corrosion is a very intriguing electrochemical phenomenon that induces aggressive changes on the metals surfaces at negative potentials. Metallic electrodes undergo extensive roughening with the additional formation of nanoparticles as corrosion by-products. Although the mechanism is not resolved, one of the likely explanations is that cathodic corrosion occurs via metastable metallic anions, which are stabilized by non-reducible electrolyte cations [30]. An innovative procedure enabling the synthesis of small metallic nanoparticles (< 5 nm) was demonstrated in the group of Koper et al. [31,32]. In their work, a strong negative potential of approximately -10 V (vs. HgO) was used to corrode a metallic wire to obtain nanoparticles dispersed into the bulk of the concentrated alkaline electrolyte solution [33]. Although the technique has great potential, it must be coupled with another synthesis steps for nanoparticles deposition on high surface-area support and it is not useful for in-situ electrocatalysts production.

Besides the issue of the production of electrocatalysts it is well-known that electrocatalysts exhibit stability problems; mostly related to the loss of electrochemical surface area due to the growth of

nanoparticles, i.e., clustering. Identified degradation mechanisms are agglomeration/coalescence/coarsening [34] and Oswald ripening [35–38]. There are ways to slow down the degradation processes by nanoparticle confinement [39–41] however these same strategies can also induce mass transport issues and blockage of the active surface area. Therefore, another application of electrocatalysis is of high interest, namely reactivation. It is known from heterogeneous catalysis as metal redispersion strategies for recycling of supported metal catalysts [42]. Redispersion is performed by exposing the catalyst to the reactive gaseous conditions that break down the particles [39,43]. No such protocol is known for the application for supported electrocatalysts in a liquid environment.

In this paper we showcase two breakthroughs:

- (i) New three-step electrodeposition protocol for the preparation of Ag, Pt, Pd, Au and Ni metallic nanoparticles with narrow particle size distribution ranging below 5 nm. We propose a novel approach for obtaining supported small metal nanoparticles by combining the well-established double-pulse electrodeposition approach with controlled cathodic corrosion in organic solvents, which disperses the nanoparticles. This new protocol enables a reliable preparation of nanoparticles reaching even down to the single atom. Thus electrodeposition is finally able to reach its full versatility potential as supported metallic electrocatalyst synthesis method.
- (ii) New metallic electrocatalysts reactivation protocol based on the cathodic corrosion phenomena is shown to effectively redisperse the degraded electrocatalyst. In this paper, we for the first time provide the solution for in-situ electrochemical regeneration of supported metal nanoparticles in a liquid. Our proof of principle is opening new and simple direction towards general in-situ liquid reactivation of nanoparticles as electrocatalysts.

2. Results and discussion

2.1. Three-step electrodeposition

Our new three-step electrochemical protocol is schematically represented in Fig. 1. In the first step, fast cathodic pulses are performed

to induce metal nucleation. We added one extra pulse to the nucleation step with the same potential and charge parameters as the first one in order to increase the number of nuclei and subsequently the surface density of metallic nanoparticles. Secondly, the relatively long growth step at less negative potential is responsible for the particle formation. The most important novelty of the current work is the addition of the final third step; the pulse at high cathodic overvoltage. It takes advantage of cathodic corrosion phenomena that breaks down and disperses the metallic nanoparticles. In contrast to Koper's protocol where nanoparticles are released to the electrolyte in our case, they stay on the electrode surface. This step is performed in new methanol electrolyte solution; importantly, without any dissolved metal precursor. With controlled cathodic corrosion, we are able to break down the relatively large (i.e., 100 nm) particles into nanoparticles (i.e., 3 nm) with a narrow particle size distribution over the whole carbon substrate.

The procedure for new three-step electrodeposition is described in the Supplementary Information Section 1. Our strategy to prepare small nanoparticles is exemplified, as a proof of concept, on the synthesis of Ag nanoparticles. In the Supplementary Information Sections 2 and 3, we additionally confirm that this procedure is indeed a general method for the preparation of small nanoparticles by also synthesizing Pt, Ni, Au and Pd nanoparticles. An organic solvent (MeOH) is chosen to slow down the growth kinetics and have more influence on particle morphology [20,29,44,45]. However, the method is not limited to MeOH as a solvent. Identical results are obtained with acetonitrile, dimethyl sulfoxide as solvents (Supplementary Information Section 1).

With the nucleation step of double pulse electrodeposition and the growth step Ag nanoparticles with an average particle size of 76 nm are obtained (see Ag1 in Table 1 and Fig. 2a). This is in accordance with the literature [16,17,28,46]. The growth of Ag nanoparticles during the double pulse electrodeposition step proceeds via a nucleation-aggregative mechanism [47]. At first in the nucleation step, silver cations are adsorbed on the surface and reduced to small silver nanoparticles. As the nanoparticles form, the rapid diffusion-controlled-growth regime is reached by depletion of the Ag ions at and near the electrode surface. After consumption of Ag ions, the Ag particles subsequently start to aggregate and recrystallize to larger particles with well-defined edges [17]. For this reason, it is practically impossible to deposit particles below approximately 10–100 nm. In Fig. 2b and c SEM results of different cathodic polarization (CP) pulses are shown: at −6 V (Ag2) and at −8 V (Ag3). We want to acknowledge that self-limited electrodeposition thin metal films have been reported on metal supports [48,49]. This perspective approach is unfortunately not suitable for the supports used in this work due to their different nature of the surface chemistry and electrodynamic behaviour.

Application of a controlled cathodic corrosion pulse on electrodeposited Ag nanoparticles of 76 nm (Ag1) gives rise to effective fragmentation and distribution of newly formed small Ag nanoparticles over the surface. Interestingly, this can be considered as the opposite electrochemical effect to the Ostwald ripening or particle coalescence and/or agglomeration. As indicated in Table 1, where parameters of the deposition and the average particle size is displayed, by applying a

Table 1
Microscopic data of as prepared Ag nanoparticles.

N°	Applied voltage (V)	Charge (mC/cm ²)	X _{size} (nm)	σ _{dia} (%)	m _{Ag} gloss (m %)
Ag1	/	/	76	29	/
Ag2	−6	0.3	29	70	< 1%
Ag3	−8	0.3	3.4	9	< 1%
Ag4	−10	0.3	2.1	14	< 1%
Ag5	−12	0.3	single atom	/	76%
Ag6	−10	0.15	11	16	< 1%
Ag7	−10	0.45	1.4	12	53%

negative pulse of −8 V (Ag3) the particle size can be lowered till approximately 3 nm. For Ag2 the pulse of −6 V (Ag2; Fig. 2b) a high standard deviation for the average particle size is found. This is caused because the nanoparticles are still dispersing into smaller nanoparticles. Therefore the process was not entirely completed. Increasing the charge passed through the surface at the same potential (−6 V) did not change the particle size or bimodal size distribution. This an indication that a critical potential (energy) is needed in order to further break down the particles. For our case, this potential is −8 V.

The dispersion phenomena of big Ag nanoparticles is directly proven in Fig. 3, where an identical location (IL) SEM images of Ag nanoparticles before and after dispersion are being shown. It can be clearly seen that big particles break down to small nanoparticles. At first impression, the amount of Ag present at the surface is smaller after cathodic polarization. However, at this magnification, SEM is at its limit of detection, and not all nanoparticles are visible (TEM is shown below in Fig. 4a and in the Supplementary Info. Fig. S2 and S3). In addition, the spreading of the newly formed nanoparticles occurs on to the support away from the viewing area. This effect is also seen in the Supplementary Info. Fig. S7. Interestingly, the newly formed nanoparticles are located on specific defects and cavities within the rough structure of the carbon support. This indicates that nanoparticles are migrating on carbon support at the cathodic conditions and finally get anchored on a carbon defect. We speculate that the process of dispersion occurs via atomic diffusion. We note that the migration of nanoparticles is not limited to the support material. Identical results can be obtained on a Ti support showing that defects in the support act as anchoring sites.

In Fig. 4 two scanning transmission electron microscopy (STEM) images of Ag4 (−10 V) and Ag5 (−12 V) samples are shown (more in Supplementary Info. S2 and S3). By applying a negative pulse of −10 V (Ag4) nanoparticles with an average size of 2.1 nm are obtained with a reasonable standard deviation. At −12 V (Ag5) the smallest obtained sizes are found. The initial nanoparticles of ca 76 nm are completely dispersed over the surface, and a significant amount of single Ag atoms can be observed. STEM investigating shows that, as already observed by the IL-SEM (Fig. 3b), the single atoms and small nanoparticles are mainly found at specific defects like edges and steps of the carbon substrate. This finding suggests that the mechanism of the dispersion effect indeed occurs through atomic surface diffusion. The migrating species are thus attached (coordinated) to the surface via carbon functional groups where they act as ligands and stabilize the single atoms. When high cathodic polarization is applied, small particles or even single atoms are charged. Such polarization in non-polar solvents causes repulsion through London forces of negatively charged electron clouds in nanoparticles and thus pushes charged parts of larger nanoparticles out. We also want to stipulate that similar results were found in other organic solvents such as acetonitrile and dimethyl sulfoxide (Supplementary Info. Section 1).

ICP-MS analysis is performed in order to further confirm that the particles disperse over the support surface and do not detach into the bulk electrolyte as in the case of Koper et al. [30,31]. Results shown in Table 1 reveal that up to a cathodic polarization pulse of −10 V, only a negligible amount of Ag is “corroded” to the electrolyte solution as a result of particle detachment. However, at the potential of −12 V, where mostly single Ag atoms are obtained, 76% of the total mass of Ag is removed. This is presumably because there are not enough ligands or defects on the carbon surface to host all of the Ag single atoms. Nevertheless, it is a still viable protocol to prepare single atom catalyst, and the Ag in the solution can be recycled and reused again in the next electrodeposition.

In addition to the potential, the parameter of the amount of charge passed through the surface was varied. The results displayed in Table 1 shows that when the charge is lowered from 0.3 mC/cm² (Ag4) to 0.15 mC/cm² (Ag6) larger particles are obtained. Further increase in the charge (0.45 mC/cm²) does not affect the particles size (Ag7). As

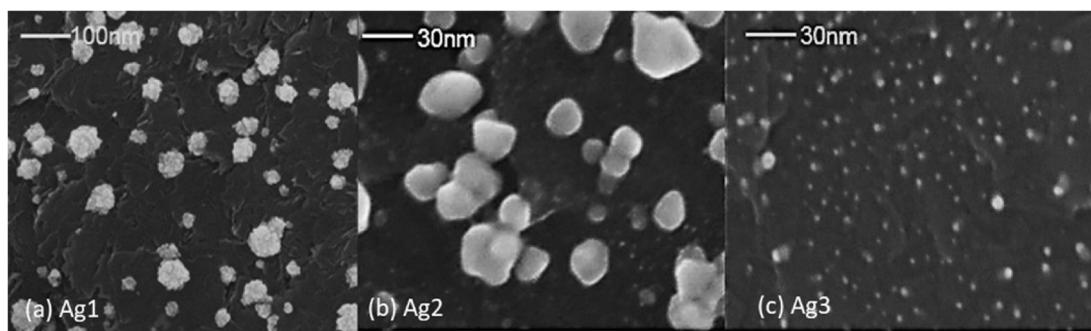


Fig. 2. SEM micrographs of Ag nanoparticles on a carbon rod (CR) after different cathodic polarization pulses; (a) Ag1 no pulse, (b) Ag2 @ -6 V and (c) Ag3 @ -8 V.

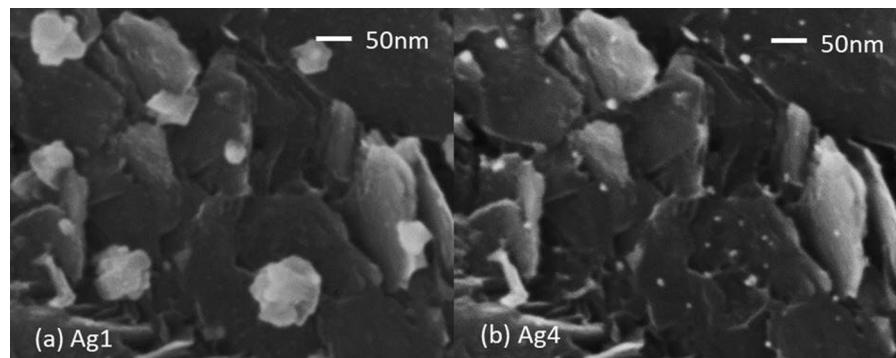


Fig. 3. IL-SEM image of the electrodeposited Ag nanoparticles before (a) and after (b) controlled cathodic corrosion pulse at -10 V.

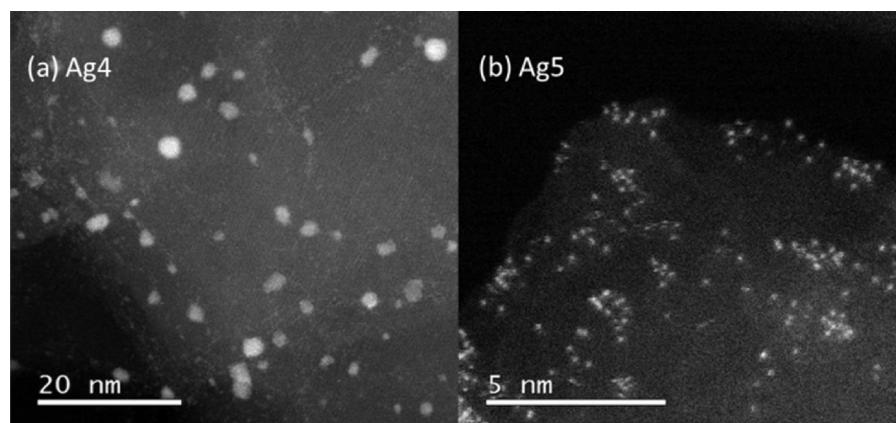


Fig. 4. TEM micrographs of Ag nanoparticles on a CR after different cathodic polarization pulses; (a) -10 V– 0.3 mC/ cm^2 and (b) -12 V– 0.3 mC/ cm^2 .

mentioned earlier, a critical potential is needed to further fragmentize the metallic nanoparticles. At -12 V this is indeed confirmed, however with the addition of Ag substantial removal (see ICP-MS results in Table 1).

The versatility of our new type of cathodic polarization based technique is exemplified for the production of several other metallic nanoparticles. Extensive results can be found in Supplementary Info. Sections 2 and 3. Pt, Ni, Au and Pt experiments exhibit the same behaviour as above-described Ag metal. However, with small variations in the potentials required for effective dispersion of electrodeposited metals. In addition, comparable results are obtained with other solvents (acetonitrile, dimethyl sulfoxide), however not without the presence of alkyl ammonium salts. Until now no effort is being made in the synthesis of nanoparticles with specific, preferential crystallographic orientations [50] or even nanoalloy [32]. Nevertheless, it is author's belief that these will all be possible by varying different experimental parameters like metal loading, cathodic pulse conditions, temperature, additional of capping agents, deposition of alloys, etc.

2.2. Redispersion

Here we show another very important application of cathodic corrosion phenomena besides the production of small metallic nanoparticles. There are, to the best of our knowledge, no procedures for *in situ* reactivation of clustered supported electrocatalysts in liquids. Interestingly, in the field of homogeneous and heterogeneous catalysis, the process of the regeneration of small, catalytically active nanoparticles from larger particles is a known practice. However these can only be applied to the catalysts in various gas phases and unsupported nanoparticles dispersed in solution; generally based on a reforming process [39,43]. With our novel cathodic polarization technique grown metallic nanoparticles are shown to be effectively redispersed on a support (processes schematically represented in Fig. 5). We note, that the mechanism of cathodic corrosion is completely different from the one used in the regeneration protocols in heterogeneous catalysis.

In Fig. 6 three SEM images are shown: (a) electrodeposited Ag nanoparticles, (b) degraded (clustered) Ag nanoparticles and (c) redispersed Ag nanoparticles via controlled cathodic polarization. With our adapted electrodeposition technique Ag nanoparticle with an average

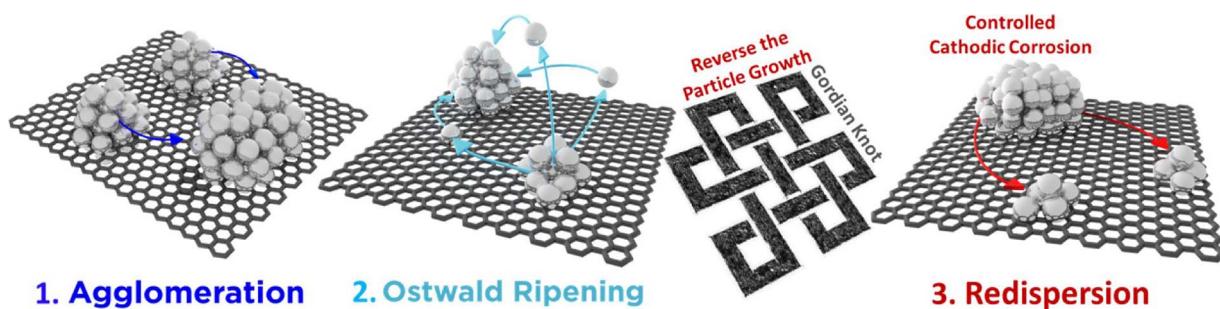


Fig. 5. Schematic representation of supported electrocatalyst degradation via particle growth, namely (1.) Agglomeration and (2.) Ostwald Ripening and the activation protocol, namely (3.) Redispersion.

particle size of are 24 nm obtained. The agglomerates are obtained by performing an electrochemical degradation protocol. The full degradation protocol is described in the Supplementary Info. Section 4. After degradation Ag particles grew to 250 nm (Fig. 6b). In the third step a cathodic polarization pulse of -10 V is set to redisperse the Ag nanoparticles on the whole surface. Results indicate that with cathodic polarization the average size of the clusters (250 nm) can be reduced to 37 nm. In addition, ICP-MS results show that a minimum of Ag ($< 5\text{ m}\%$) is lost with cathodic polarization. In the Supplementary Info. Section 4 we have added IL-SEM images (Fig. S6) to confirm the dispersion effect on clustered nanoparticles.

To show that the electrodeposited nanoparticles are electrochemically active we performed a simple electrochemical experiment by studying the formation of oxides. In Fig. 7 the surface electrochemistry (first cycle) of Ag1 and Ag4 samples is studied in an alkaline solution. (In Supplementary Info. Section 4, we additionally show a long-term CV experiment up to 15.000 cycles). Metal oxidation and reduction capacitive currents are directly proportional to the metal active surface area. It can be clearly seen that after cathodic pulse at -10 V Ag1 surface areas increase (Ag4). This is in complete agreement with the fact that big nanoparticles break down to smaller nanoparticles where utilization of surface area per mass is higher.

We now established that a controlled cathodic corrosion gives rise to a dispersion of metallic nanoparticles that can be used for electrodeposition of small nanoparticles or redispersion of degraded clustered electrocatalysts. In our opinion the process of dispersion can be caused by two phenomena. Firstly, studies have shown that the use of tetraalkyl ammonium salts or in our case TBAP (supporting electrolyte) facilitates corrosion [31,51,52]. When the electrode is at high negative potential, the positively charged ion (tetrabutyl ammonium ion) is being attracted and subsequently reduced at the electrode to an unstable tetrabutyl ammonium intermediate. This compound aids in the formation of metal complexes and metal hydrides [31] and could act as a capping agent. Both are unstable and decompose rapidly under AC bias. It is our belief that well defined short pulses give rise to decomposition of these intermediates without particle detachment. Dispersion is not effective without TBAP as supporting electrolyte. Although a supporting electrolyte is required, other quaternary ammonium salts such as tetrabutyl ammonium bromide also give rise to cathodic

dispersion. It is known that specific interaction of electrolyte cations is crucial actors in the cathodic corrosion process [30]. Secondly, such extreme potentials cause vigorous reduction of the solvent (MeOH) to methane. The production of methane could possibly aid in the production of short-lived reactive intermediates which decompose quickly. The experimentally determined cathodic polarization pulse to disperse larger nanoparticles has presumably a thermodynamic character because it is determined by the stability of the formed reactive intermediates. However, the cathodic polarization pulse is not a standard equilibrium potential since one would require accurate knowledge of all involved intermediates and reactants. This is, however, a part of our ongoing future studies.

3. Conclusions

In summary, we have successfully demonstrated the effect of electrochemical dispersion (breaking down) of metallic nanoparticles via controlled cathodic corrosion treatment. It is shown that by applying a sufficiently negative potentials metallic nanoparticles could be dispersed into smaller nanoparticles and even single atoms over a conductive substrate. This procedure was effectively exemplified on (i) electrochemically synthesized electrodeposited Ag nanoparticles with the average size of 76 nm and (ii) degraded Ag nanoparticles with the average size of 250 nm in an organic electrolyte solution of MeOH and tetrabutylammonium perchlorate. The method of cathodic polarization is very versatile and can also be applied to Pt, Ni, Au and Pd, and in other solvents (acetonitrile and dimethylsulfoxide), support material (Ti) and supporting electrolyte (tetrabutyl ammonium bromide). By optimizing the voltage and charge of the cathodic polarization pulses, the final size of nanoparticles could be controlled. With a polarization pulse of -10 V , the smallest nanoparticles with a particle size reaching down to the single atom level were obtained. These findings were confirmed by ICP-MS analysis of the electrolyte where no significant amount of silver was found ($< 0.001\text{ mg}$). Our novel in-situ electrochemical treatment can be considered as a general way to break down and disperse supported metallic nanoparticles for the purposes of electrodeposition synthesis and degraded electrocatalysts reactivation.

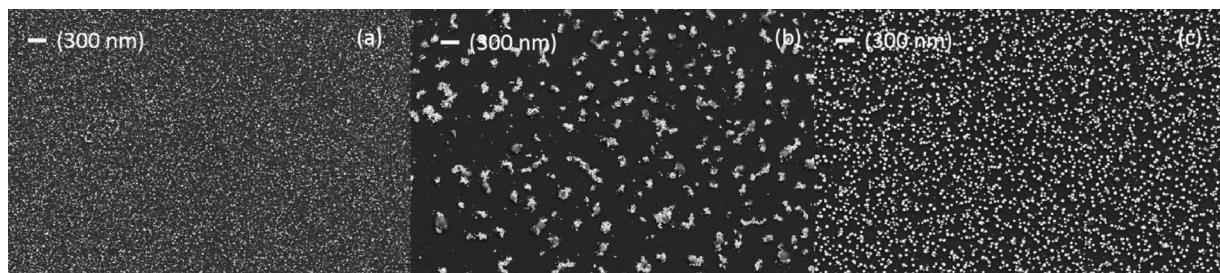


Fig. 6. SEM images of (a) electrodeposited Ag nanoparticles (b) clustered nanoparticles after electrochemical cycling (c) dispersed Ag nanoparticles after cathodic polarization.

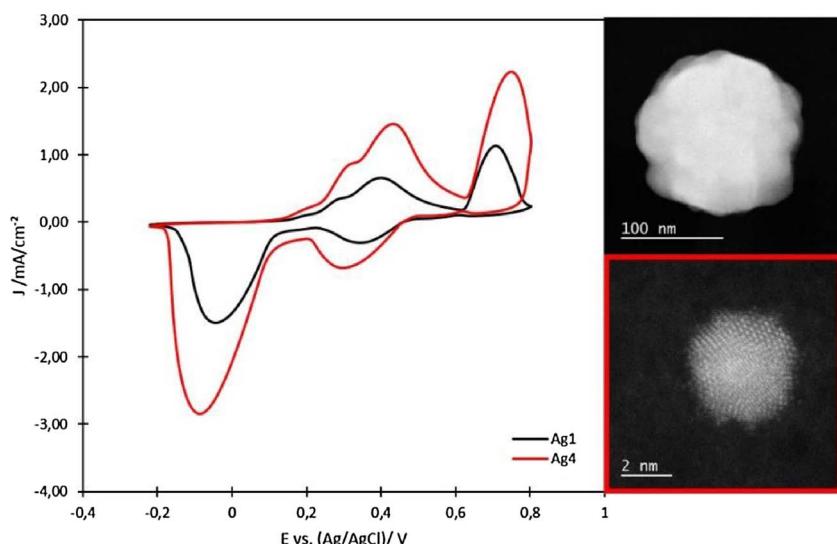


Fig. 7. CV features of Ag1 (no cathodic pulse) and Ag4 (−10 V) in alkaline solution of NaOH (0.1 M) obtained at 50 mV s^{−1}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.080>.

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